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## DEADHESION MECHANISM OF COMMERCIAL UNPIGMENTED EPOXY AND ALKYD COATING UNDER CATHODIC POLARISATION

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### ABSTRACT

*The wet adhesion behavior of epoxy-polyamide, and alkyd organic coating on silane modified mild steel surface has been studied in an earlier work. Results indicated that 3-Glycidoxypropyltrimethoxy silane (3-GPS) enhanced the wet adhesion of epoxy-polyamide coating and 3-Aminopropyltrirthoxy silane (3-APS) enhanced the wet adhesion of alkyd coating with cohesive failure mode towards the end of the experiment. Cathodic disbonding experiments on these systems indicated that the enhanced adhesion for alkyd, has no effect on their cathodic disbonding behaviour while the use of 3-GPS to enhanced the adhesion of epoxy-polyamide greatly reduced its rate of cathodic disbanding.*

*Keywords: cathodic disbonding, epoxy-polyamide, alkyd, 3-Aminopropyltrirthoxy silane, 3-Glycidoxypropyltrimethoxy silane, wet adhesion.*

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### 1. INTRODUCTION

It is a well known fact that the relationship between the wet adhesion strength to the cathodic disbonding behavior of an organic coating can never be straightforward. The known reason for this is the fact that whiles the adhesion phenomenon is dependent on the integrity of the interfacial region especially towards chemical attack, most cathodic disbondment processes involved the

destruction of this region possibly by chemical attack<sup>1</sup> or other mechanisms<sup>2</sup>. As such, a simple relationship between adhesion and cathodic disbondment is very difficult to establish.

Nevertheless, results from this study, does indicate that in at least one coating system, enhancing the wet adhesion strength through chemically pre-treating the substrate with silane compounds does seem to increase its resistant towards cathodic disbondment. On the other hand

however, in the other worked system, there was no significant influence of the increased wet adhesion strength to the cathodic disbondment failure.

From these observations, it seems that one cannot generalize the mechanisms involved in the disbondment of organic coatings under cathodic polarization, and perhaps more importantly, whether these mechanisms will at all be affected by the wet adhesion strength of the coating.

## 2. EXPERIMENTAL METHODS

The mild steel substrates used in these experiments were mild steel panels (Q-Panels), with dimension 15 cm by 8 cm obtained from Q-Panel Co. They have been ground to a finish of FEPA European P-Series # P150 or equivalent nominal grain diameter of 90 to 100 micrometers according to ASTM A366 Q95698. All steel samples were first washed with 5% Neutracon<sup>®</sup> solution before thoroughly rinsing with deionised water. They were then degreased twice in acetone followed by ethanol and finally washed thoroughly with deionised

water. The samples were then allowed to dry at room temperature for at least four hours before used. Commercial non-pigmented, single, clear and real coatings were used in this study. They were the commercial non-pigmented two-pack polyamide cured epoxide and clear alkyd.

Surface pre-treatment conditions with 3-aminopropyltriethoxy silane (99%) (3-APS), 3-glycidoxypolytrimethoxy silane (96%) (3-GPS) were fixed for all the mild steel substrate under study. These silane compounds were chosen based on the amino and epoxy functional groups that they possess respectively, and were found to enhance the wet adhesion strength of the organic coatings under study<sup>3</sup>. The silane and ethanol were obtained Aldrich Chemical Company. The treating solution used for hydrolysing the silane molecules was that of 1/1 (v/v) ethanol/water solution. It was first prepared and allowed to settle in a sealed container for at least 30 minutes before use. All the silane solutions used in the experiments were treated at 2% v/v in this solution. The solutions were thoroughly mixed and stored for 24 hours in a dark cupboard before application. The final pH values of the silane solutions are listed in Table 1.

**Table 1.** List of systems and pretreatments used in the study

Silane	pH
3-aminopropyltriethoxysilane	10.5
3-glycidoxypolytrimethoxysilane	5.63

Silane pre-treatments were carried out by first rinsing the panels for 30 seconds with the intended silane solution from a wash bottle. They were then left to dry at room temperature for 2 hours. Coatings were subsequently applied soon after complete drying of the panels.

The cathodic disbonding test set up was done in accordance to the British Standard 3900: Part F10, except for the variation in the electrolyte and the method of introducing the holiday.

Electrical connections were accomplished by firmly attaching an insulated conducting wire with nut and bolts. An artificial holiday measuring 1 mm in diameter was introduced mechanically using a small drill on each panel before starting the test. Six panels of each coating system were polarised potentiostatically at -1000 mV versus the standard calomel electrode in 3.5% sodium chloride solution. The disbonded data obtained for each coating system was therefore represented by a mean value taken from the six readings. The potential of each electrode were checked and adjusted twice daily with an independent standard calomel reference electrode.

Three types of plots were used in analysing the cathodic disbonding behaviour of the coating systems<sup>4,6</sup>. They were the disbonded area versus

time, square root of area versus time and square root of area versus square root of time. In all the systems, the disbonded area is almost circular in nature. Therefore a plot of square root of disbonded area versus square root of time is proportional to the plot of average disbonded distance from the defect versus square root of time since the radius of the circle represents the distance from the defect.

In order to determine the area of coating disbonded, a non-destructive test method was adopted. As the difference in colour tone between the disbonded regions to that of the intact area was very obvious for all the coating system examined, it was then used to indicate the area of disbondment. The panels were removed according to a set time interval. They were quickly rinsed with deionised water with care taken not to damage the coating. The area disbonded was traced on an acetate film, which was then cut and weighed. In order to relate the weight to an area of the film, a sample of thirty squares with an area of 1 cm<sup>2</sup> each, were cut at random from six separate acetate films of the same type. Five squares were obtained from each film. Each of these squares was weighted and their mean value and standard deviation was calculated. Finally the mean value obtained was used to calculate the actual area of delamination of the coating using the following formula:

$$\text{Disbonded area (cm}^2\text{)} = \frac{\text{Weight of film (g)}}{0.01425 \text{ (g cm}^{-2}\text{)}} \quad (1)$$

At the end of the experiment, the coatings were cut radially with a scalpel from the artificial defect in order to confirm the delamination front. From this test it was confirmed that the visual difference in colour of the disbonded coating, can be used to indicate the disbonded area.

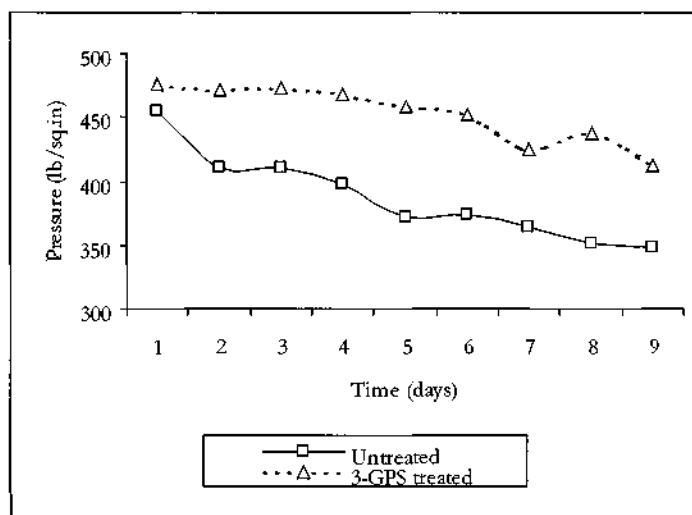
### 3. RESULTS AND DISCUSSION

#### 3.1 Cathodic disbonding of epoxy-polyamide coating system

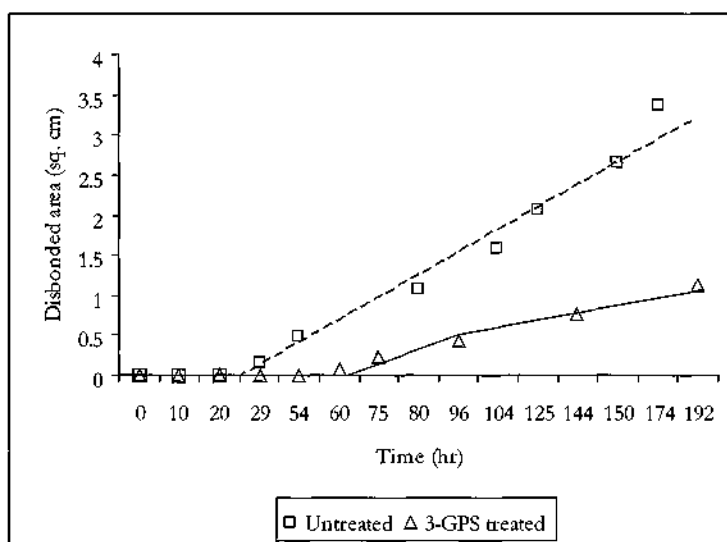
Earlier studies confirmed that pre-treatment of mild steel with 3-GPS increases the wet adhesion strength of epoxy-polyamide when compared to the untreated system and this is shown in Figure 1. The overall increase in the

wet adhesion strength was maintained through out the whole duration of experiment with a significant difference in adhesion "pull off" values even at day nine. Closer looks at the trend, reveals the overall reduction rate in adhesion of the untreated panels were infact faster than that of the treated panels through out the experiment.

The cathodic disbonding tests on these systems were conducted according to the method described earlier. The results are shown in Figure 2. Although fresh new samples were prepared for this test, it must be emphasized that in all the experiment, the thickness of the coating was kept constant.



**Figure 1:** The wet adhesion strength of epoxy-polyamide on 3-GPS pre-treated mild steel when compared to the untreated system



**Figure 2:** The relationship between the disbonded area of epoxy-polyamide coating on mild steel with and without 3-GPS pre-treatment

The result indicates that there is a “delay time”<sup>7</sup> where no immediate disbonding for both systems. Disbondment was first observed after 29 hours for the untreated system and about 60 hours for the treated system. The results also indicated a mean area of 3.52 cm<sup>2</sup> was disbonded for the untreated system in 192 hours, while, an average area of only 1.13 cm<sup>2</sup> was disbonded for the treated system within the same duration of experiment. This means that the rate of disbondment for the untreated system is in the region of 0.018 cm<sup>2</sup>/hr while that of the 3-GPS treated system is  $5.87 \times 10^{-3}$  cm<sup>2</sup>/hr. This also means that the untreated panel is disbonding at about three times much faster than that of the treated panels.

The plot of the square root of disbonded area versus time for epoxy polyamide system is shown in Figure 3. The plot indicates that for epoxy on

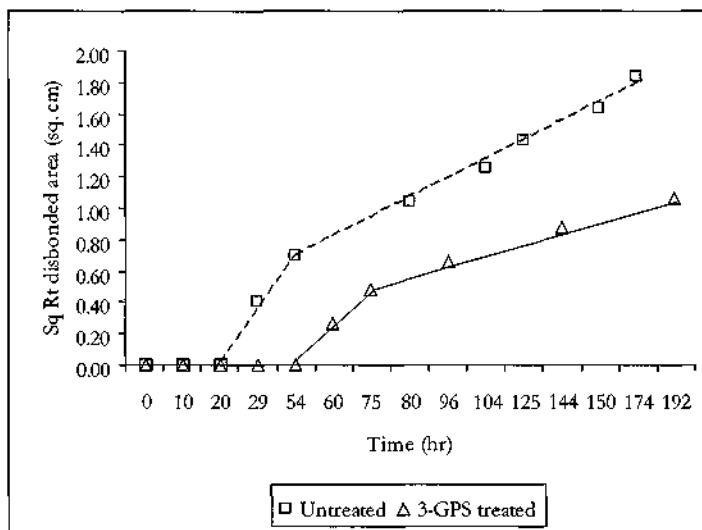
non treated mild steel, the disbonding distance with time relationship is parabolic at the beginning especially until the 80th hour at which it appears to become more towards linear with time. A similar trend was noticed for the treated system, however the more linear trend was seen after the 96th hour.

These behaviours may be linked to the parabolic kinetic behaviour of disbonding, in which the rate of disbondment slows down, as the disbondment front gets further away from the defect<sup>8</sup>. It is a known fact that the transport of cations and oxygen is required to support the cathodic reduction reaction and has also been recognized as one of the major contribution towards determining the rate of cathodic disbonding at this working potential and environment<sup>9</sup>. As such, a parabolic relationship of the disbonding distant with time, may suggest that the transport of these species is along the

coating/substrate interface, which may require more time as the disbonding front gets further away from the defect. However, after the 80th hour, the relationship becomes more towards linear for the untreated system. This means that the disbonding rate is no longer much affected by the distance of the delaminating front from the defect, but rather on the time of "exposure" to the experimental conditions. In order for this to happen, the cations and the oxygen will have to reach the disbonding front through the coating. This phenomenon is thought to be likely, as long exposure of the coating system to the aqueous environment may allow water to be transmitted through the coating and thus develop pathways for the transport of ionic species<sup>10-13</sup>. By the same argument, the phenomenon is also apparent for the epoxy on 3-GPS pre-treated system

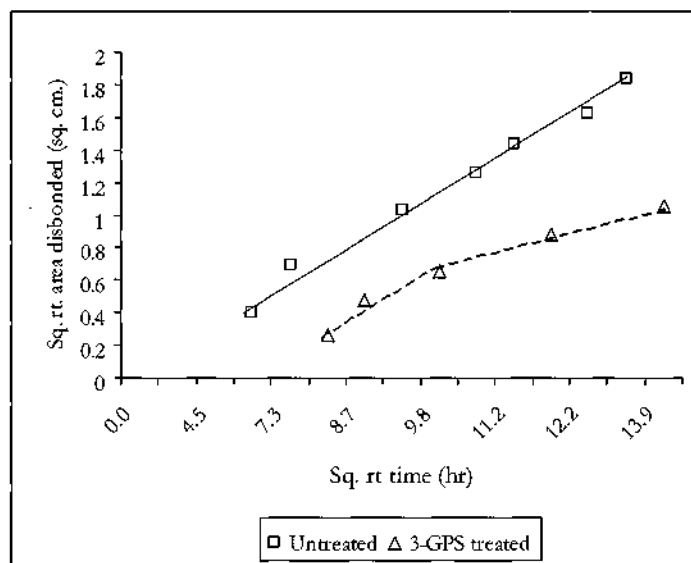
except that the parabolic relationship occurred until the 96th hour and then appears to tend towards a more linear relationship after that. However, even though the linear trend is dominant towards the end of the experiment, the fact still remains that 3-GPS enhanced the resistance towards cathodic disbanding of epoxy polyamide.

The plot of the square root of disbonded area versus square root of time is shown in Figure 4. A linear plot was observed for the untreated systems, confirming the parabolic shape of the square root area versus time plot. A tending towards a linear relationship of the square root area versus time plot after the 80th hour is however not very apparent from this plot. Nevertheless, it is believed that if the time of exposure is prolonged, this behaviour may become more apparent.



**Figure 3:** Plot of the square root of disbonded area versus time for epoxy polyamide coating system on mild steel with and without 3-GPS pre-treatment





**Figure 4:** Plot of the square root of disbonded area versus square root of time for epoxy polyamide coating system on mild steel with and without 3-GPS pre-treatment

As for the epoxy-polyamide coating system on the 3-GPS treated substrate, the plot of square root of disbonded area versus square root of time (Figure 4), shows two linear relationship with different slopes. One until the 96th hour and another slope after that hour. By the same argument, this linear relationship indicates that the plot of square root of area versus time is parabolic and that a cationic transport along the coating interface is the controlling factor in determining the rate of disbonding (i.e a parabolic kinetic). Before the 96th hour, the slope of the 3-GPS treated system and the untreated system appears to be almost the same, thus the rate of disbonding after initiation appears to be almost the same as the untreated system, although the delay time in the former is longer. However, after the 96th hour, the rate of disbondment of

the 3-GPS treated system appears to be slower than that of the untreated system. A possible explanation is that, at and near the defect, the structure of the interfacial region may not be the real representative of the true interfacial structure brought about by the 3-GPS pre-treatment, due to possible mechanical stress related damage done to it during the introduction of the defect. Thus as the disbondment front gets further away from the defect, the interfacial region is more in its true form and therefore possibly represent the actual effect of the adhesion enhancement by the 3-GPS on the rate of disbonding.

Nevertheless, it can be concluded from this data that the 3-GPS pre-treatment slows down the cathodic disbondment of the epoxy-polyamide coating. The "delay time" is also increased by the 3-GPS pre-treatment. This is possibly related to the time required by the water to weaken the

“stronger” interfacial region before allowing disbonding process to begin.

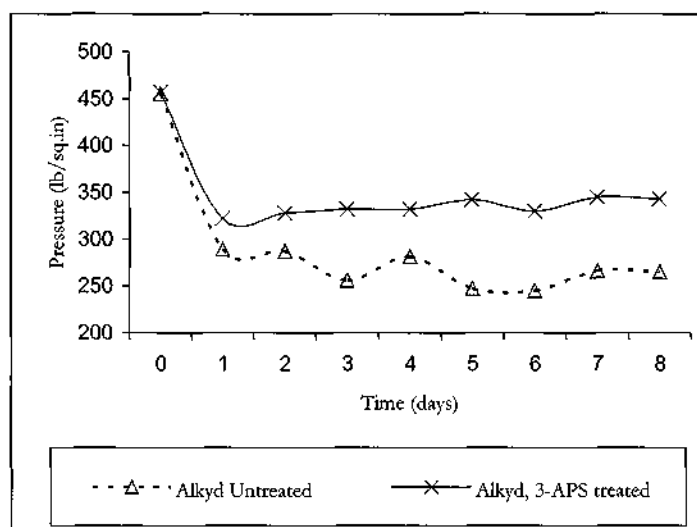
### 3.2 Cathodic disbondment of alkyd

Comparison of the wet adhesion strength for both alkyd and on untreated and 3-APS treated mild substrate was described in earlier experiment. From Figure 5, it is clear that 3-APS enhanced the wet adhesion of both the coatings on mild steel.

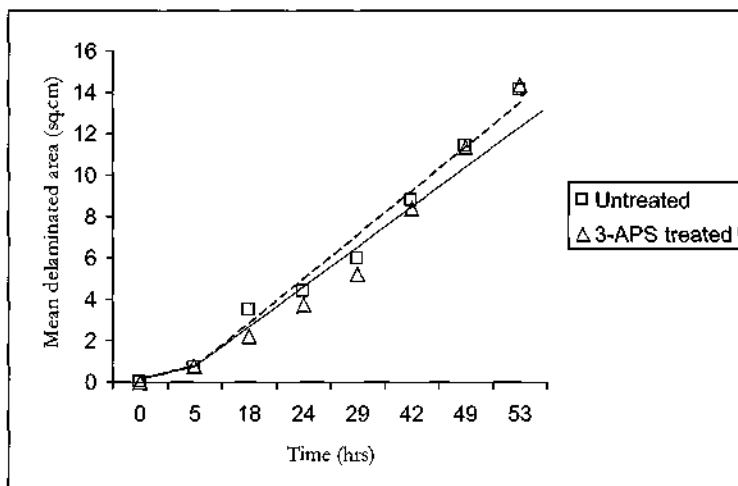
However, results for cathodic disbondment behaviour obtained from this work indicated that the

disbondment rate of the alkyd was not affected by the adhesion enhancement caused by the 3-APS pre-treatment. This can be seen from Figure 6.

The figure indicated clearly that there is no significant effect of the 3-APS pre-treatment on the overall disbondment of alkyd coating on mild steel. Infact, since the disbonding rate for the coating systems on the control untreated panels is the same as that of the 3-APS treated system, it is believed that the controlling factor determining the cathodic disbonding is also the same.



**Figure 5:** Wet adhesion strength of alkyd on mild steel with and without 3-APS pre-treatment



**Figure 6:** The relationship between the disbonded areas of the alkyd on mild steel with and without 3-APS pre-treatment

The mechanisms of cathodic disbondment have been quite well established. Thus, an alkaline environment under the coating when the substrate is cathodically polarised has been identified to have a deleterious effect on adhesion of coatings. In addition, polymer coatings whose binders are prone to attack by the hydroxyl ions are known to degrade chemically, and this could lead to the destruction of interfacial interaction leading to disbondment<sup>14</sup>.

Earlier reviews indicated that ester based coatings like the alkyds are known to degrade in an alkaline medium. Thus polymer degradation due to alkaline environment is also likely to occur for this system.

One possibility therefore as to why the disbonding rate of the alkyd on 3-APS is the same as that of untreated panels is because it possibly underwent

coating degradation leading to the destruction of the interfacial chemical interaction. Therefore, if the adhesion enhancement was brought about by secondary interactions of intact ester carbonyl groups to that of the acidic hydrogen of the silanols, as hypothesised earlier, the “destruction” of these ester groups by alkaline hydrolysis (which convert them to carboxylate anions) and the destruction of the polymer structure may lead towards the destruction of the interactions. This mechanism need not be adhesion dependent.

#### 4. CONCLUSION

A positive conclusion that can be drawn from the data is that the alkyd whether on untreated or on the 3-APS pre-treated substrate disbonded at the same rate. The disbonding behaviour for all the systems is more towards a linear kinetic type of behaviour and there is no link to its adhesion behaviour. The disbonding rate

is constant even though when the disbondment front gets further away from the defect, a phenomenon indicating towards a through coating transport mechanism of the cations and oxygen<sup>15</sup>. As both these coatings are less resistance to chemical chemical attack and that the disbonding behaviours are both towards linear kinetic, it is believed that coating coating degradation is the main controlling factor in the disbonding behaviour.

On the other hand, the results of the cathodic disbonding of epoxy-polyamide coating system indicates that the disbonding rate is slower for the system with 3-GPS pre-treatment. As argued earlier, oxide dissolution cannot be the major mechanism involved in the disbonding of the epoxy-polyamide system as if this is the case then both the epoxy on untreated panel and 3-GPS treated panel would have disbanded at the same rate. Neither can it be due to aqueous displacement as pre-treatment by 3-GPS increases the wet adhesion strength of the epoxy-polyamide. As such it seems that the adhesion enhancement brought about by 3-GPS pre-treatment increases its resistance towards cathodic delamination. The enhancement in adhesion may be brought about by the primary bond formation between the epoxy groups of the silane with that of the polyamide groups. If this is true, then the silane will become part of the polymer matrix bonded by primary covalent bonds. Therefore it seems

that the establishment of these primary chemical bonds may contribute towards the reduction rate of cathodic disbondment.

A factor that must be pointed out from these results is the fact that the disbonding behaviours of both the epoxy coating on the non-treated and the 3-GPS treated mild steel are more towards a parabolic kinetic type of behaviour. The disbonding behaviours are adhesion dependent with the epoxy on the 3-GPS pre-treated substrate disbond at a slower rate. For both the coating systems, the disbonding rate gets slower at the disbondment front gets further away from the defect. This phenomenon is more related to the interfacial coating transport mechanism of the cations and oxygen. Unlike in the alkyd and system, it is difficult to relate the disbonding behaviour to a chemical degradation phenomenon, as we would expect the epoxy coating to be far more resistant to chemical attack. Since the behaviour is adhesion dependent, it is possible that the disbondment is due to a mechanical failure like the osmotic rupturing due to alkaline environment<sup>16</sup>. In this case, the migration of cations towards the cathodic region to neutralise the OH<sup>-</sup> ions produced during the cathodic reduction reaction will increase the osmotic pressure underneath the coating leading towards a mechanical rupturing of the interfacial region.

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